Science of the Total Environment 639 (2018) 258–262

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Short Communication

A modified method of high molecular weight adsorbable organic chlorine measurement in saline water: Dialysis pretreatment

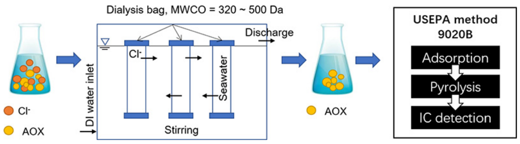
Jiajian Liu [a,1], Li Ling [a,b,1], Yi Li [c], Chao Wang [b,*], Chii Shang [a,d,**]

[a] Department of Civil and Environmental Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong
[b] Faculty of Science and Technology, Technological and Higher Education Institute of Hong Kong, Hong Kong
[c] Key Laboratory of Integrated Regulation and Resource Development of Shallow Lakes, Ministry of Education, College of Environment, Hohai University, Nanjing, PR China
[d] Hong Kong Branch of Chinese National Engineering Research Center for Control & Treatment of Heavy Metal Pollution, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong

HIGHLIGHTS

- Adsorbable organic chlorine (AOCl) measurement in seawater was inaccurate.
- Dialysis pretreatment can eliminate the interference of chloride.
- Total flushing water at volumetric ratio of 1200:1 removes over 99% chloride.
- AOCl detainment by dialysis membrane depends on its molecular weight cutoff.
- The modified method can be used in chlorinated seawater at pH 6.5 to 10.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 21 March 2018
Received in revised form 11 May 2018
Accepted 13 May 2018
Available online 19 May 2018

Editor: Dr F Frederic Coulon

Keywords:
Seawater
Adsorbable organic chlorine
Chlorination
Dialysis

ABSTRACT

Adsorbable organic halogen is a mean to quantify total organic halogen, which is an important toxicity indicator in disinfection byproduct studies. However, quantification of low concentrations of adsorbable organic chlorine (AOCl) formation in seawater chlorination using the USEPA Method 9020B was found inaccurate due to the presence of high concentrations of chloride. In this study, a dialysis-based pretreatment technique was proposed, optimized and adopted to eliminate the interference of chloride in quantifying low concentrations of AOCl in seawater. A volumetric ratio of dialysis samples to continuous-flow deionized water at 1:1200 was found sufficient to remove over 99% of chloride. As a result, chloride to AOCl ratios can be reduced to less than 20,000, and the interference from chloride can thus be eliminated. The detainment of AOCl by the dialysis pretreatment depends on the molecular weight cutoff of the cellulose seamless dialysis membrane currently used, which was determined to be around 320 to 500 Da. The dialysis pretreatment can be used to measure AOCl concentrations in chlorinated seawater samples at pH 6.5 to 10.

1. Introduction

Chlorination of seawater is important to prevent biofilm growth on pipelines in seawater cooling, toilet flushing and desalination systems, to inhibit biofouling of reverse osmosis membranes, and to inactivate pathogens in seawater swimming pool, marine aquaculture and ship ballast water (Kim et al., 2009; Matin et al., 2011; Khalanski and Jenner, 2012; Werschkun et al., 2012; Gong and Zhang, 2015; Zhang

---

* Corresponding author.
** Correspondence to: C. Shang, Department of Civil and Environmental Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong.
E-mail addresses: chaowang@vtc.edu.hk (C. Wang), cechii@ust.hk (C. Shang).
[1] Shared first authorship.

https://doi.org/10.1016/j.scitotenv.2018.05.160
0048-9697/

et al., 2015; Manasfi et al., 2017). However, chlorination of seawater forms disinfection byproducts (DBPs) that pose potential health, aesthetic and ecological risks (Agus and Sedlak, 2010; Werschkun et al., 2012; Gong and Zhang, 2015; Kim et al., 2015; Le Roux et al., 2015; Zhang et al., 2015; Manasfi et al., 2017; Richardson and Ternes, 2017). Major DBPs formed in seawater chlorination are halogenated DBPs, e.g., chlorinated, brominated and iodinated DBPs (Kim et al., 2015; Le Roux et al., 2015). Except the known low molecular weight (MW) DBPs measured by gas chromatography, a large portion of unknown, high MW halogenated DBPs remain unaccounted for (Krasner et al., 2006). A collective parameter, total organic halogen (TOX), has been used to determine the overall concentrations of the known low MW DBPs and the mass abundant unknown but toxicologically important high MW halogenated DBPs in drinking water and wastewater (Hua and Reckhow, 2006; Li et al., 2010; Kristiana et al., 2015; Li and Mitch, 2017).

TOX can be specified into purgeable organic halogen (POX), extractable organic halogen (EOX), and adsorbable organic halogen (AOX) according to their extraction procedures. POX is a collective measurement of volatile organic halogens that can be purged from water samples based on the USEPA Method 9021 (USEPA, 1992). EOX measures the organic halogens in solid samples such as soil, sediment and sewage sludge based on the USEPA Method 9023 (Reemtsma and Jekel, 1996; USEPA, 1996). Although EOX has been used to measure organic halogens in seawater samples (Manasfi et al., 2017), a significant loss of organic halogens, which have high polarities and low partition coefficients between the organic solvents and water, may occur during the extraction process (Han et al., 2017). On the other hand, AOX measures organic halogens that are adsorbed by granular activated carbon (GAC) in drinking water and ground water with the USEPA Method 9020B (USEPA, 1994). AOX is commonly adopted for measuring TOX, including both polar and non-polar halogenated DBPs in water sources (Oleksy-Frenzel et al., 2000; Hua and Reckhow, 2006; Kristiana et al., 2015). AOX includes adsorbable organic chlorine (AOCl), adsorbable organic bromine (AOBr), and adsorbable organic iodine (AOI).

The measurement of AOX requires a series of sample pretreatment procedures, including adsorption of AOX onto two GAC columns in series, desorption of inorganic halides present on the columns and pyrolysis, before detection (USEPA, 1994; Gong and Zhang, 2013). The USEPA Method 9020B requires that the second-column measurement should not exceed 10% of the two-column total measurement to ensure that the first column has enough sites to adsorb most of the organic halogens. The method also specifies that the ratio between halides and organic halogens in samples shall be less than 20,000 to avoid the competition of the adsorption sites between halides and organic halogens. However, the ratios between chloride and AOCl in chlorinated seawater samples are over 38,000 as calculated from the reported concentrations of halogenated DBPs including trihalomethanes, haloacetic acids and haloacetonitriles (Agus and Sedlak, 2010; Kim et al., 2015; Le Roux et al., 2015). Therefore, the adsorption of organic chlorine in chlorinated seawater samples onto GAC cartridges may be interfered by chloride. On the other hand, the ratios between Br^- and AOBr and those between I^- and AOI in chlorinated seawater samples are approximately 120 and 10, respectively, as estimated from the reported concentrations (Agus and Sedlak, 2010; Kim et al., 2015; Le Roux et al., 2015), suggesting that AOBr and AOI can be measured by the USEPA Method 9020B.

The chloride interference may be reduced by 1) desorption of chloride on GAC cartridges; and 2) removal of chloride from samples. It is reported that the chloride interference in a chlorinated saline wastewater effluent could be minimized by increasing the volume of the nitrate rinsing solution to 40 mL (Li et al., 2017). However, Hua and Reckhow (2006) reported a loss of AOX (22.4%) in the desorption of chloride when increasing the volume of the nitrate rinsing solution to 30 mL, meanwhile, the weakly adsorbed organic chlorine was washed out (Reckhow et al., 2008). Li et al. (2010) suggested the use of silver nitrate ($AgNO_3$) to reduce high levels of chloride in chlorinated Suwannee River fulvic acid samples by forming silver chloride (AgCl) precipitant. However, the process could be expensive considering the high $AgNO_3$ concentrations needed to reduce chloride concentrations in seawater. Dialysis pretreatment is another way to reduce chloride concentrations in seawater samples, because dialysis removes low molecular weight compounds based on the concentration gradients and nominal molecular weight cut-off (MWCO) of the dialysis membrane. The dialysis pretreatment has been used to remove dissolved inorganic nitrogen (DIN) to reduce its interference to dissolved organic nitrogen (DON) measurement in waters, with the common ratios of DIN to DON in the range of 0.6 to 15.6 (Lee and Westerhoff, 2004; Li et al., 2010). Whether the use of dialysis pretreatment can reduce the chloride interference when measuring AOCl in waters with high initial Cl^-/AOCl ratios requires confirmation.

The objectives of this study were thus to 1) illustrate the limitation of the USEPA method in measuring AOCl in high salinity water, 2) standardize dialysis pretreatment protocol, and 3) test the dialysis pretreatment in measuring AOCl in chlorinated seawater at different pHs.

2. Materials and methods

2.1. Chemicals and solutions

Details on the chemicals and solutions used in this study are given in Text S1 (Supporting Information).

2.2. Experimental procedures

Seawater was collected and filtered prior to use, and details are provided in Text S2 (Supporting Information). The filtered seawater was used for the subsequent AOX measurement. Trichlorophenol (TCP) dissolved in double deionized water with various sodium chloride (NaCl) concentrations (0, 11,500 and 19,000 mg/L as Cl^-) was used to simulate seawater fed to seawater desalination using reverse osmosis processes.

Dialysis pretreatment protocol was optimized. Samples were placed in pretreated dialysis bags (details on the pretreatment of dialysis bags are given in Text S3, Supporting Information) with 12 cm in length. An extra 20% length of the dialysis bags was provided to avoid rupturing the bags due to drawing water into the bags by osmotic pressure. Air in the dialysis bags was squeezed out, and the bags were then sealed with Teflon-lined lids. The dialysis bags were immersed into the deionized (DI) water tank with a constant water flow at 500 mL/min in and out of the water tank. The increase of the sample volume in the bag after dialysis was recorded to calculate the dilution factor. The dialysates were then subjected to AOCl and chloride measurement. Filtered seawater halide removal experiment was conducted at various rinsing durations. The volumetric ratio of the rinsing water to samples was calculated by the cumulative rinsing volume (duration time × DI water flow rate) divided by the total sample volume (number of samples × the volume of each sample) and it varied from 400:1 to 4800:1. The chloride removal efficiency of dialysis was calculated by chloride concentration in the dialysate over its concentration in filtered seawater. The optimal ratio of 1200:1 was selected for further tests.

The claimed MWCO of the dialysis bag is 100 to 500 Da. To narrow down MWCO of the dialysis bag, various compounds with molecular weights ranging from 100 to 700 Da were used. Dichloroacetonitrile (DCAN, MW = 110 Da), trichloroacetonitrile (TCAN, MW = 144 Da), bromodichloroacetonitrile (BDAN, MW = 189 Da), dibromoacetonitrile (DBAN, MW = 233 Da), methylene blue (MW = 320 Da) and potassium indigo trisulfonate (MW = 616 Da) were tested separately using dialysis. After dialysis, the remaining percentage of the model compounds in the dialysis bags with a volumetric ratio of total flushing water to samples of 1200:1 was used to determine the MWCO of the dialysis bag.